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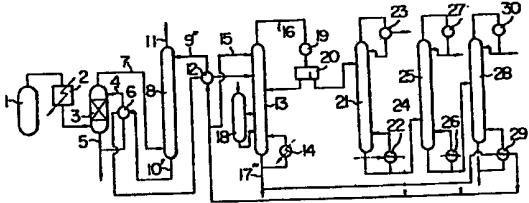
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⑤5 Process for producing unsaturated nitrile.

⑤5 A process for producing an unsaturated nitrile comprising the steps of water-cooling, in a quenching column, a reaction mixture containing the unsaturated nitrile, a saturated nitrile and prussic acid, said reaction mixture being obtained by ammoniation of an olefin, absorbing the reaction mixture with the absorption water in an absorption column, subjecting the resulting absorption solution to extractive distillation in a stripping column by using solvent water, taking out a distillate containing the crude unsaturated nitrile and prussic acid from the top of the stripping column, and then removing the prussic acid, water and the like from the distillate by distillation in distillation columns of a de-prussic acid column, a dehydration column and a product column to obtain the unsaturated nitrile, wherein the solvent water obtained from the lower part of the stripping column and being substantially free from the unsaturated nitrile and prussic acid contained in the feed to the stripping column is recycled as the absorption water in the absorption column or the solvent water effluent from the acetonitrile-stripping column obtained by feeding the solvent water withdrawn from the lower part of the said stripping column to remove acetonitrile substantially is recycled as the solvent water in the stripping column and/or the absorption water in the absorption column, characterized in that when the absorption solution effluent from the stripping column is preheated with the solvent water withdrawn

from the lower part of the stripping column and/or the solvent water withdrawn from the lower part of the acetonitrile-stripping column and then fed to the stripping column, the absorption solution is preheated by previously passing the same through at least one column selected from the group consisting of the cooler for the circulating water in the quenching column, the condenser for the overhead vapor in the stripping column, the condenser for the overhead vapor in the dehydrating column, and the condenser for the overhead vapor in the product column, and the solvent water is used, prior to pre-heating the above absorption solution, as a heat source of at least one column selected from the distillation columns in the de-prussic acid column, the dehydration column and the product column.



PROCESS FOR PRODUCING UNSATURATED NITRILE

1 This invention relates to a process for pro-
2 ducing an unsaturated nitrile by ammoxidation of an ole-
3 fin, for example, a process for producing acrylonitrile
4 or methacrylonitrile by ammoxidation of propylene or
5 isobutylene.

6 The object of this invention is to provide
7 a production process having a very high energy effi-
8 ciency in which sensible or latent heat at a relatively
9 low temperature generated in the production system which
10 heat has never been able to be utilized is converted to
11 a cooling or heating heat-source and effectively
12 utilized.

13 In the process for the production of an unsa-
14 turated nitrile by ammoxidation of an olefin, the reac-
15 tion products at a high temperature are cooled with
16 water and then absorbed in a large amount of water (for
17 example, according to Japanese Patent Publication No.
18 657/66, absorption water is used in an amount of 17.8
19 times the weight of acrylonitrile), after which the
20 resulting absorption solution is repeatedly subjected to
21 distillation by heating and condensation by cooling,
22 whereby the unsaturated nitrile is separated and
23 purified from the by-products and the unreacted
24 materials. Therefore, the energy required for heating
25 and cooling has heretofore been very much and the pro-

1 portion of energy expense in the cost has been high.

The conventional process and the present process are concretely explained below referring to the accompanying drawings, in which Figs. 1 and 2 are flow sheets showing the conventional processes for producing acrylonitrile and Figs. 3, 4, 5 and 6 flow sheets showing the processes of this invention which appear hereinafter. In the drawings, 1 ... a reactor, 2 ... a heat exchanger, 3 ... a quenching column, 4 ... a line, 5 ... a line, 6 ... a cooler, 7 ... a line, 8 ... an absorption column, 9 ... a line, 9' ... a line, 9" ... a line, 10 ... a line, 10' ... a line, 10" ... a line, 11 ... a line, 12 ... a heat exchanger, 13 ... a recovery column, 14 ... a reboiler, 15 ... a line, 15' ... a line, 15" ... a line, 16 ... a line, 17 ... a line, 17' ... a line, 17" ... a line, 18 ... an acetonitrile-stripping column, 19 ... a condenser, 20 ... a decanter, 21 ... a de-prussic acid column, 22 ... a reboiler, 23 ... a condenser, 24 ... a line, 25 ... a dehydration column, 26 ... a reboiler, 27 ... a condenser, 28 ... a product column, 29 ... a reboiler, and 30 ... a condenser.

In Fig. 1, in a reactor 1, continuously fed propylene, ammonia and air undergo ammoxidation in the gas phase at a high temperature in the presence of an oxidation catalyst to give a mixture of unreacted compounds and reaction products such as acrylonitrile, acetonitrile, prussic acid and high boiling organic matters. This gaseous mixture at a high temperature is sent via a heat

1 exchanger 2 to a quenching column 3, and brought into
contact with circulating water for cooling which is
flowing down via a line 4 from the top of the column to
be cooled to a low temperature. In this cooling
5 step, the high boiling organic matters and the water
generated are incorporated into the circulating water to
be removed, and if necessary, a mineral acid is added to
the circulating water to remove the unreacted ammonia in
the reaction product gas. The heated circulating water
10 is withdrawn from the bottom of the column through a
line 5, cooled in a cooler 6, and then circulated and
fed through a line 4 to the top of the column again, and
a part of it is then eliminated from the system.

The gas introduced from the top of the
15 quenching column 3 through a line 7 to the lower part of
an absorption column 8 is contacted with the absorption
water fed via a line 9 which flows down in the column
from the top thereof, and the acrylonitrile, aceto-
nitrile and prussic acid are absorbed into the absorp-
tion water. The resulting absorption solution is taken
20 out as a bottom stream through a line 10, and the unab-
sorbed gas is discharged from the top of the column
through a line 11.

The absorption solution is passed through a
25 heat exchanger 12, heated therein, fed to a recovery
column 13 from a somewhat upper part thereof, and then
heated by means of a reboiler 14. The recovery column
usually has at least 50, preferably 60 to 100 trays, and

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1 the absorption solution is countercurrently contacted
with the solvent water sent via a line 15 to the top of
the column to undergo extractive distillation. Crude
acrylonitrile vapor containing prussic acid and water is
5 distilled out from the top of the column via a line 16,
while the solvent water is taken out from the bottom of
the column via a line 17. Most of the acetonitrile in
the absorption solution is separated by distillation in
an acetonitrile-stripping column 18 attached to the
10 recovery column 13. The solvent water substantially
free from the acetonitrile which has been taken out
through the line 17 is sent via the line 15 to the
recovery column 13, while a part thereof is passed
through the heat exchanger 12 to be cooled and then fed
15 as absorption water via the line 9 to the absorption
column 8. The crude acrylonitrile vapor distilled out
through the line 16 is cooled in a condenser 19, and the
condensate is separated into an oily layer and an
aqueous layer in a decanter 20. The oily layer is sent
20 to a de-prussic acid column 21, and the aqueous layer is
returned to the recovery column 13.

The de-prussic acid column 21 is heated by
means of a reboiler 22, and prussic acid is taken out by
distillation from the top of the column and then sub-
25 jected to fractional condensation in a condenser 23,
whereby prussic acid vapor is separated. The bottom
stream is sent through a line 24 to a dehydration column

1 25. The dehydration column 25 is heated by means of a
reboiler 26, and the vapor taken out by distillation
from the top of the column is condensed in a condenser
27, and separated into an oily layer and an aqueous
5 layer, after which the oily layer is dehydrated. The
bottom stream is sent to a product column 28. The product
column 28 is heated by means of a reboiler 29, and the
vapor taken out by distillation from the top of the
column is condensed in a condenser 30 to obtain acrylo-
10 nitrile having the desired quality, while the bottom
stream is discharged.

The conventional process for producing acrylo-
nitrile is as described above, and involves many heating
steps and cooling steps. That is to say, the recovery
15 column 13, the de-prussic acid column 21, the dehydra-
tion column 25 and the product column 28 are equipped
with the reboilers 14, 22, 26 and 29, respectively, and the
condensers 19, 23, 27 and 30, respectively, and the
quenching column 3 is equipped with the cooler 6. In
20 order to increase the energy efficiency of the process
in which heating and cooling are repeated, various coun-
termeasures have heretofore been taken. For example,
according to Japanese Patent Application Kokai
(Laid-Open) No. 81,848/80, it has been proposed that
25 solvent water at a high temperature (110° to 130°C)
taken out of the recovery column is used as a reboiler
heat source for the de-prussic acid column and the pro-

1 duct column, after which the absorption solution is pre-
heated in the heat exchanger 12 and used as the absorp-
tion water. However, this method has been disadvan-
tageous in that since the solvent water becomes cooled,
5 the quantity of heat becomes insufficient for preheating
(in the heat exchanger 12 in Fig. 1) the absorption
water to be fed to the recovery column 13, so that an
extra heat source for the recovery column (the reboiler
14) is needed, or in that the heat-conductive area of
10 the heat exchanger 12 has to be made extremely large.

In Fig. 2, the same procedure as in Fig. 1 is
repeated, except that a part of the solvent water is
withdrawn through a line 15' without being passed
through the acetonitrile-stripping column and is passed
15 through the heat-exchanger 12 to lower the temperature
of the solvent water, and then is fed to the absorption
column 8 as the absorption water through a line 9',
while the solvent water is withdrawn from the bottom
through a line 17' and sent to the recovery column 13.

20 This invention has been made in view of the situa-
tion described above, and the gist thereof is a process for
producing an unsaturated nitrile comprising the steps of
water-cooling, in a quenching column, a reaction mixture
containing the unsaturated nitrile, a saturated nitrile
25 and prussic acid which mixture is obtained by ammoni-
cation of an olefin, absorbing the reaction mixture with
absorption water in an absorption column, subjecting the

1 resulting absorption solution to extractive distillation
in a recovery column by using solvent water, taking out
a distillate containing the crude unsaturated nitrile
and prussic acid from the top of the recovery column,
5 and then separating prussic acid, water and the like
from the distillate by distillation in distillation
columns such as a de-prussic acid column, a dehydration
column and a product column to obtain the unsaturated
nitrile, and recycling, as the absorption water in the
10 absorption column and as the solvent water in the
recovery column, the solvent water obtained from the
lower part of the recovery column, free from aceto-
nitrile, which process is characterized in that when the
absorption solution effluent from the absorption column
15 is preheated with the solvent water free from aceto-
nitrile and then fed to the recovery column, said
absorption water is preheated by previously passing it
through at least one member selected from the group con-
sisting of the cooler for the circulating water in the
20 quenching column and the condensers for overhead vapors
of the dehydration column, the product column and the
recovery column, while said solvent water is used as a
heat source for at least one column selected from the
group consisting of distillation columns such as de-
25 prussic acid column, dehydration column and product
column before preheating said absorption water. That is
to say, this invention is characterized in that the

1 absorption water taken out of the absorption column is
preheated by passing it through (i) the cooler for the
circulating water in the quenching column, (ii) the con-
denser for overhead vapor of the recovery column, (iii)
5 the condenser for overhead vapor of the dehydration
column, and (vi) the condenser for overhead vapor of the
product column, and in that the solvent water effluent
from the bottom of the recovery column is used as a
heat source for at least one column selected from the
10 group consisting of (i) the de-prussic acid column, (ii)
the dehydration column, and (iii) the product column,
and then heat-exchanged with the aforesaid preheated
absorption water. Therefore, the solvent water from the
bottom of the recovery column is not only utilized as a
15 heat source for at least one member selected from the
group consisting of the de-prussic acid column, the
dehydration column, and the product column, but also
heat-exchanged with the preheated absorption water,
whereby the absorption solution can be preheated to the
20 desired temperature. Accordingly, no extra heat source
for distillation in the recovery column is needed and
that it is not necessary to improve the capacity of the
heat-exchanger to preheat the absorption solution.

On the other hand, the absorption solution
25 effluent from the absorption column at a low temperature
is passed through at least one column selected from the
group consisting of the cooler for the circulating water

1 in the quenching column and the condensers of the
distillation columns, and utilized for cooling the cir-
culating water and for condensing the overhead vapor,
and hence regeneration energy for the cooling water used
5 can be saved.

That is to say, it has been found that when
the absorption water from the absorption column is
passed through at least one column selected from the
group consisting of the above-mentioned cooler and con-
densers, there can be obtained a stable process by which
10 the solvent water from the bottom of the recovery column
can be utilized as a heat source for at least one column
selected from the group consisting of the de-prussic
acid column, the dehydration column and the product
15 column, so that the heat energy can very effectively be
saved.

The quality of the product in the steps in the
present process is not affected at all.

A preferable process of this invention is
20 explained below referring to the drawings.

As shown in Fig. 3, the absorption solution at
15° to 35°C effluent from the absorption column 8 is
passed through the cooler 6 for the circulating water in
the quenching column 3 and heated to 35° to 50°C with
25 the circulating water heated to 30° to 60°C before being
preheated with the solvent water in the heat exchanger
12. On the other hand, the solvent water at 100° to

1 120°C effluent from the bottom of the recovery column 13 is used as a heat source for the reboiler 29 of the product column 28, and then passed through the heat exchanger 12 for preheating the absorption solution, to 5 preheat the absorption solution to 70° to 90°C, which is then fed to the recovery column 13.

As a result, the heat sources can be reduced by utilizing the solvent water effluent from the recovery column as a heat source for the product column 28.

10 At the same time, the absorption solution can be preheated to such a suitable temperature as before without any substantial increase of the capacity of the heat exchanger 12, so that no extra heat source for the recovery column is needed.

15 The cooling water for the cooler 6 in the quenching column 3 can be saved as much as the quantity of heat recovered as described above.

In this process, as described above, the solvent water effluent from the recovery column 13 is 20 used as a heat source for the reboiler 29 of the product column 28, though it may be further used also as a heat source for one or more distillation columns such as the de-prussic acid column 21 and the dehydration column 25.

As shown in Fig. 4, the absorption solution at 25 15° to 35°C effluent from the absorption column 8 is passed through the condenser 19 of the recovery column 13 and heated to 35° to 50°C with the sensible heat and

1 latent heat of overhead vapor at 70° to 90°C in the
recovery column before being preheated with the solvent
water in the heat exchanger 12. On the other hand, the
solvent water at 100° to 130°C effluent from the bottom
5 of the recovery column 13 is used as a heat source for
the reboiler 29 of the product column 28, and then
passed through the heat exchanger 12 for preheating the
absorption solution, to preheat the absorption solution
to 70° to 90°C, which is then fed to the recovery
10 column 13.

As a result, the heat sources can be reduced
by utilizing the solvent water effluent from the
recovery column as a heat source for the product column
28. At the same time, the utilization of the sensible
15 heat and latent heat of the overhead vapor in the top of
the recovery column 13 makes it possible to preheat the
absorption solution to such a suitable temperature as
before without any substantial increase of the capacity
of the heat exchanger 12, so that no extra heat source
20 for the recovery column is needed. Moreover, the
cooling water for the condenser 19 becomes unnecessary.
In this process, as described above, the solvent water
effluent from the recovery column 13 is used as a heat
source for the reboiler 29 of the product column 28,
25 though it may be further used also as a heat source for
one or more distillation columns such as the de-prussic
acid column 21 and the dehydration column 25. Although

1 as described above, the absorption solution from the absorption column is preheated with the overhead vapor in the recovery column, the same effect can be obtained by preheating it with overhead vapor in the dehydration 5 column 25 or the product column 28. It may be preheated stepwise with two or more kinds of overhead vapors.

As shown in Fig. 5, the absorption solution effluent from the absorption column 8 is, prior to being preheated with the solvent water in the heat-exchanger 10 12, passed through the cooler 6 for the circulating water in the quenching column 3 to elevate the temperature of the absorption water with the circulating water having an elevated temperature. On the other hand, the high temperature solvent water substantially 15 freed from the unsaturated nitrile and prussic acid contained in the feed to the recovery column withdrawn from the side of the recovery column 13 through the line 15" without passing through the acetonitrile-stripping column is used as a heat source for the reboiler 29 in 20 the product column 28, and thereafter passed through the heat exchanger for preheating the absorption solution to preheat the absorption solution, after which the absorption solution thus preheated is fed to the recovery column 13.

25 As a result, the solvent water effluent from the recovery column can be utilized as the heat source in the product column 28 to save the heat source. At

1 the same time, the absorption solution can be preheated
to an optimum temperature without substantially
increasing the capacity of the heat-exchanger 12, so
that no extra heat source for the recovery column is
5 needed. Moreover, the cooling water for the cooler 6 in
the quenching column 3 is remarkably saved.

In this example, the solvent water effluent
from the recovery column 13 is used as the heat source
of the reboiler 29 in the product column. However, it
10 may also be used as a heat source of at least one of the
distillation columns of the de-prussic acid column 21,
the dehydration column 25 and the like.

As shown in Fig. 6, the absorption solution
effluent from the absorption column 8 is, prior to being
15 preheated with the solvent water in the heat exchanger
12, passed through the condenser 19 in the recovery
column 13 to elevate the temperature thereof with the
sensible or latent heat of the overhead vapor of the
recovery column. On the other hand, the high tem-
20 perature solvent water withdrawn from the side part of
the recovery column without passing through the
acetonitrile-stripping column and substantially freed
from the fraction comprising the unsaturated nitrile and
prussic acid contained in the feed to the recovery
25 column is used as the heat source of the reboiler 29 in
the product column 28, and thereafter passed through the
heat exchanger 12 for preheating the absorption solution

- 1 to preheat the absorption solution, after which the absorption solution is sent to the recovery column 13.

As a result thereof, the solvent water

effluent from the recovery column is utilized as the

- 5 heat source of the product column 28, whereby the saving of heat source is made possible, and at the same time, the absorption solution can be preheated to an optimum temperature without increasing the capacity of the heat exchanger 12, so that no extra heat source for the recovery column is needed. In addition, the cooling water for the condenser 19 in the recovery column is made unnecessary.
- 10

In this example, the solvent water is used as

the heat source of the product column 28 and may also be

- 15 used as a heat source of at least one of the distillation columns of the de-prussic acid column, the dehydration column 25 and the like. Moreover, in this example, the absorption solution is preheated with the overhead vapor of the recovery column, but may also be preheated
- 20 with the overhead vapor of the dehydrated column 25 or the product column 28 to obtain a similar effect.

Furthermore, it may be preheated at multiple stages with at least two overhead vapors.

This invention is as described above, and

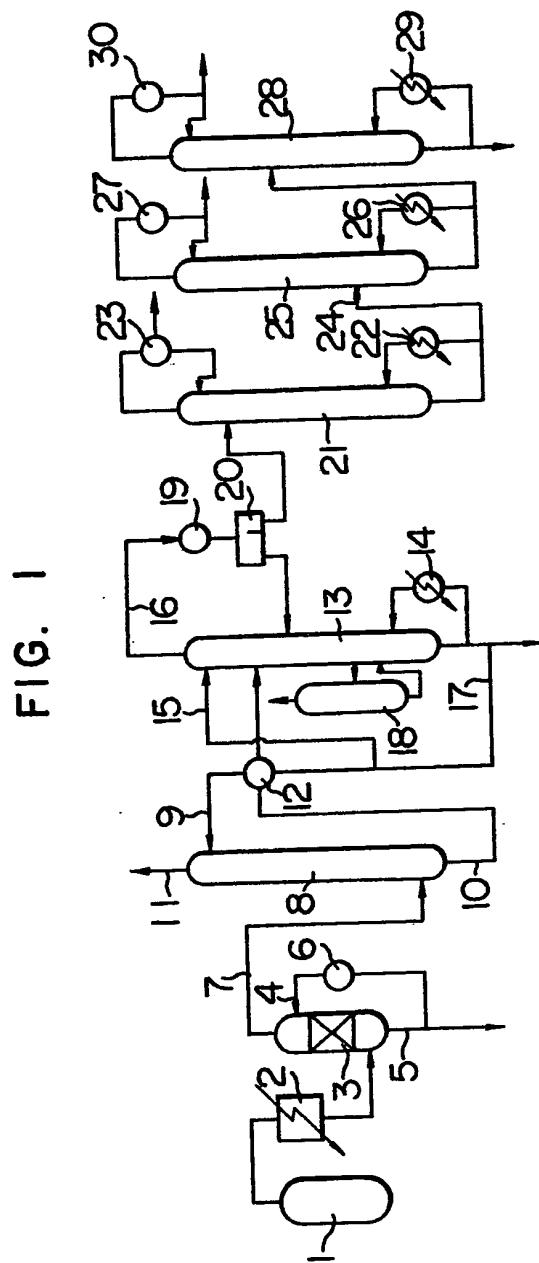
- 25 enables the reduction of the heat sources for the distillation columns such as the de-prussic acid column, the dehydration column and the product column and the

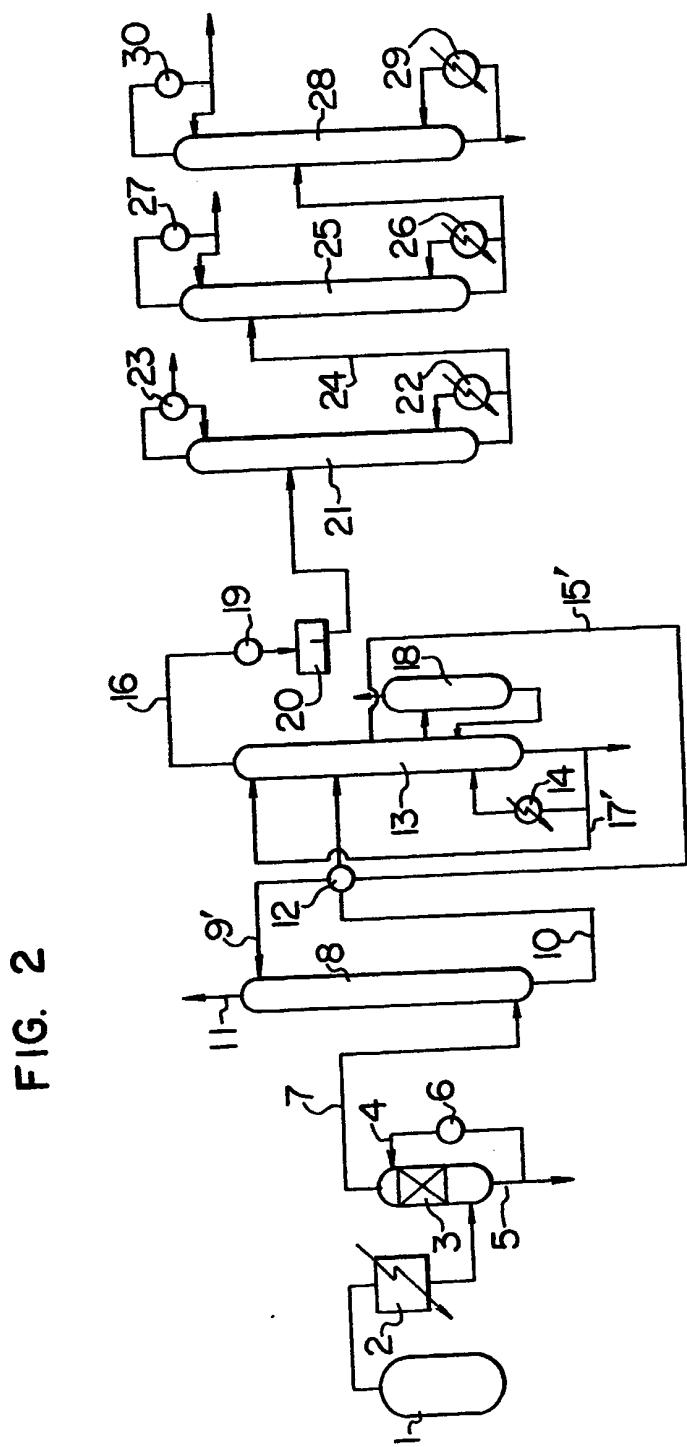
1 saving of the heat source for the recovery column, and
hence requires substantially no increase of the capacity
of the heat exchanger for preheating the absorption
solution. Furthermore, the cooling water for the cir-
5 culating water in the quenching column and the cooling
water for condensation in distillation columns such as
the recovery column, the dehydration column and the
product column can be saved, and therefore, the energy
efficiency can greatly be improved.

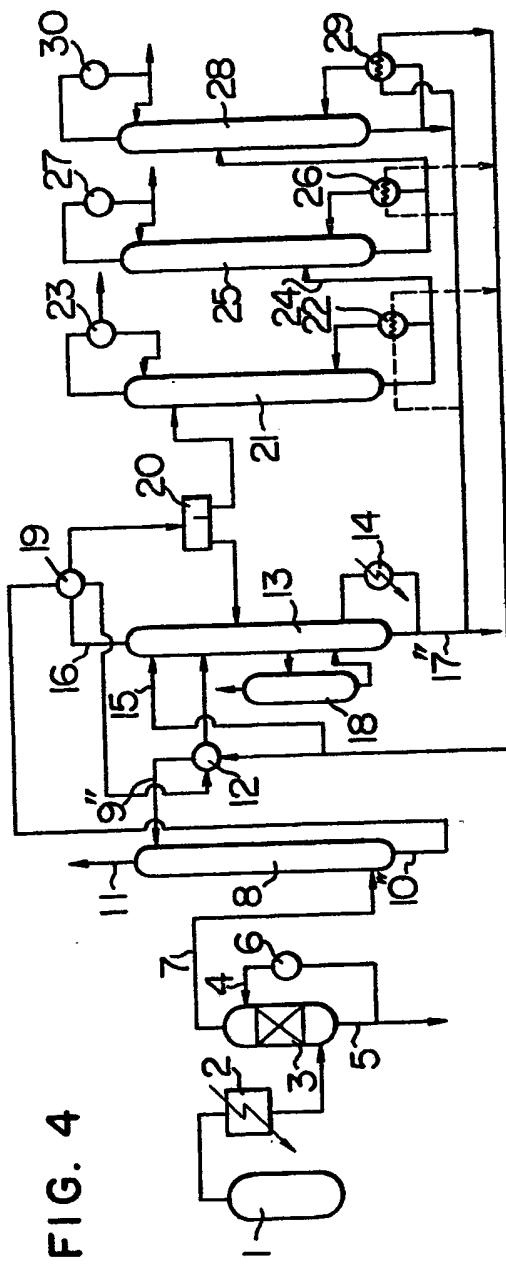
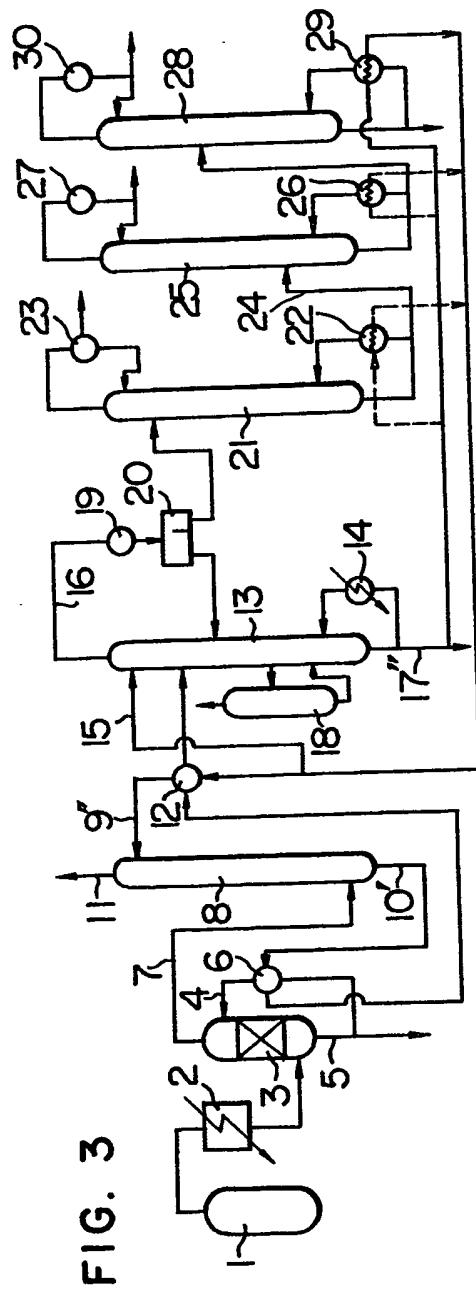
WHAT IS CLAIMED IS

1. A process for producing an unsaturated nitrile comprising the steps of water-cooling, in a quenching column, a reaction mixture containing the unsaturated nitrile, a saturated nitrile and prussic acid which mixture is obtained by ammonoxidation of an olefin, absorbing the reaction mixture with the absorption water in an absorption column, subjecting the resulting absorption solution to extractive distillation in a recovery column by using solvent water, taking out a distillate containing the unsaturated nitrile and prussic acid from the top of the recovery column, and then separating prussic acid, water and the like from the distillate by distillation in distillation columns of a de-prussic acid column, a dehydration column and a product column to obtain the unsaturated nitrile, wherein the solvent water obtained from the side part of the recovery column substantially free from the unsaturated nitrile and prussic acid contained in the feed to the recovery column is recycled as the absorption water in the absorption column, or the solvent water withdrawn from the lower part of the said recovery column is fed to the acetonitrile-stripping column to remove substantially all the acetonitrile, and the thus obtained solvent water is recycled as the solvent water in the recovery column and/or as the absorption water in the absorption column, characterized in that when the absorption solu-

tion effluent from the absorption column is preheated with the aforesaid solvent water withdrawn from the lower part of the recovery column and/or the solvent water withdrawn from the side part of the recovery column without passing through the acetonitrile stripping column, and then fed to the recovery column, said absorption solution is preheated by previously passing it through at least one column selected from the group consisting of the cooler for the circulating water in the quenching column, the condenser for the overhead vapor in the recovery column, the condenser for the overhead vapor in the dehydration column and the condenser for the overhead vapor in the product column, and the above-mentioned solvent water is used as a heat source for at least one column selected from the group consisting of distillation columns of the de-prussic acid column, the dehydration column, and the product column before preheating said absorption solution with the solvent water.







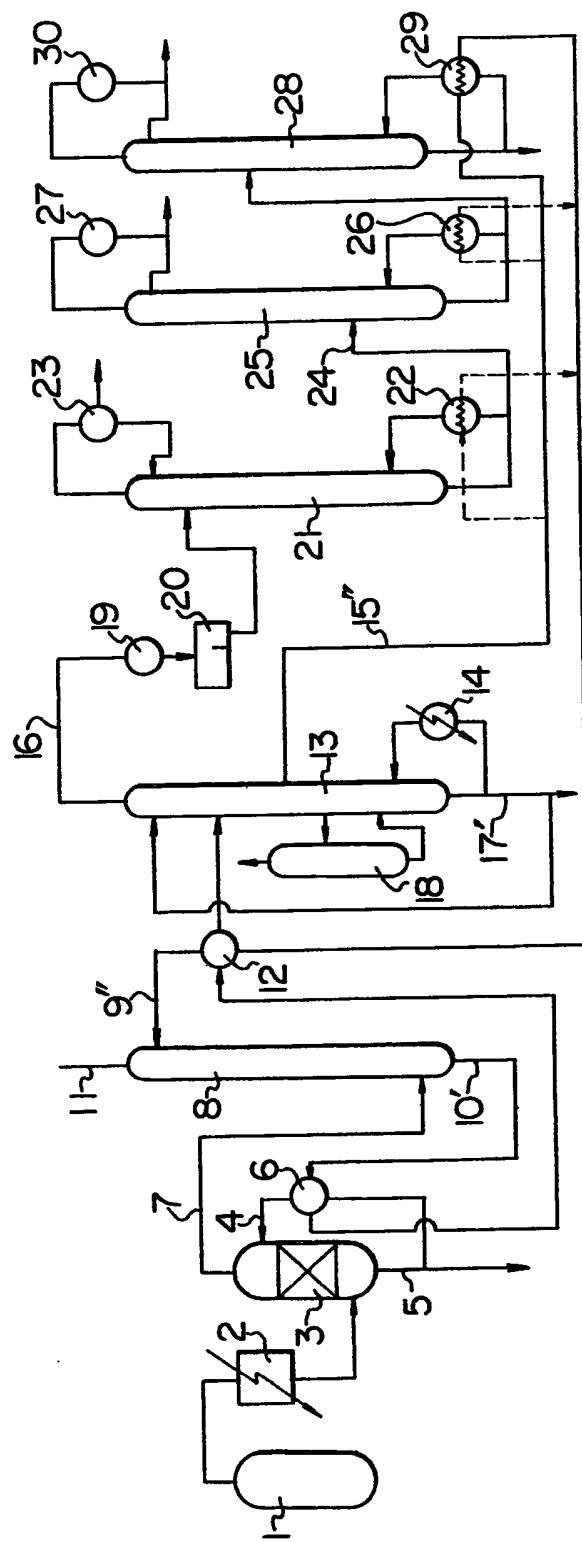
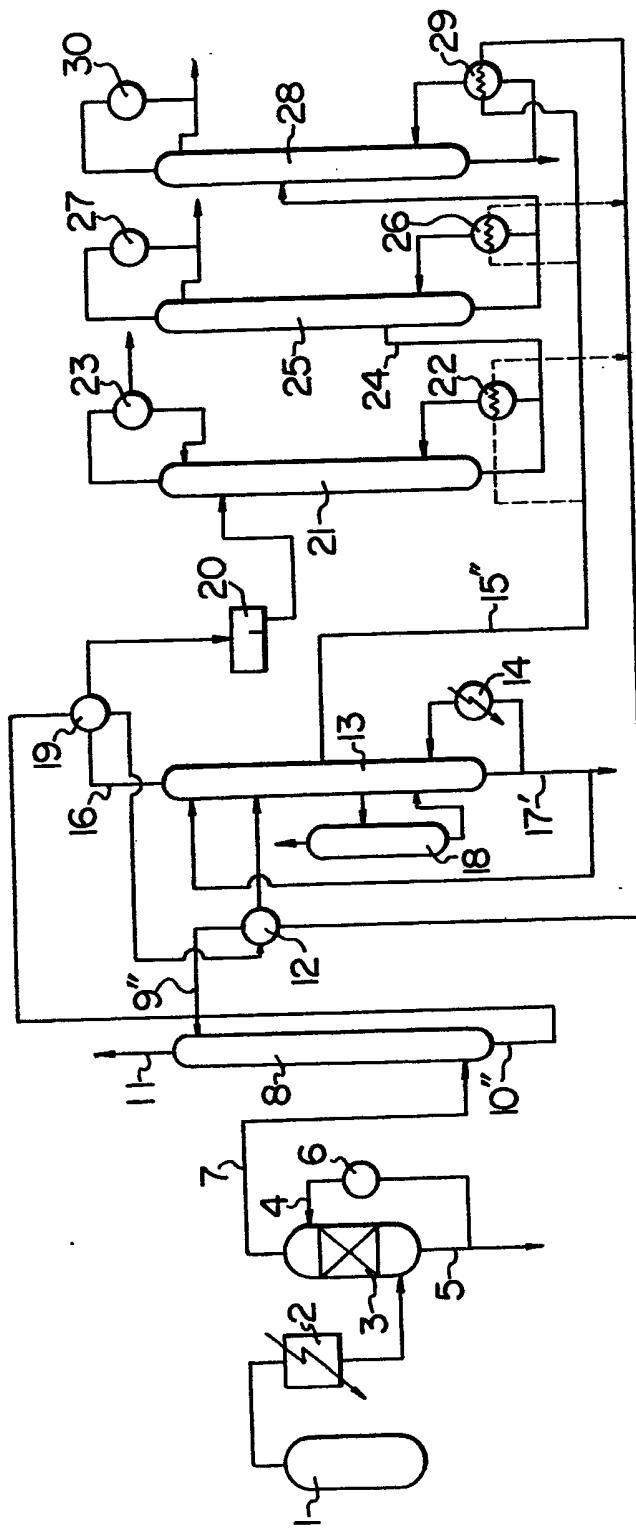


FIG. 5

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FIG. 6





European Patent
Office

EUROPEAN SEARCH REPORT

0053518
Application number

EP 81 30 5681.9

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3) |
|---|--|-------------------|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| X | <p><u>EP - A2 - 0 012 039</u> (STANDARD OIL CO.) * claims 1 to 7; page 2, lines 13 to 19; page 3, paragraph c; fig. *</p> <p>—</p> | 1 | <p>C 07 C 120/14 C 07 C 121/32</p> |
| A | <p><u>US - A - 3 895 050</u> (BADGER CO.) * column 5, line 24; column 6, lines 12 to 15 *</p> <p>—</p> | | <p>TECHNICAL FIELDS SEARCHED (Int.Cl. 3)</p> |
| A | <p><u>DE - A - 1 593 357</u> (SOCIETA EDISON) * page 9, line 1; example 1 *</p> <p>—</p> | | <p>C 07 C 120/14 C 07 C 121/32</p> |
| | | | <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p> |
| <p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p> | | | |
| Place of search | Date of completion of the search | Examiner | |
| Berlin | 24-02-1982 | BREW | |